

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of Kazunori KANEDA et. al.

Application No.: 10/598,688

Filed: May 14, 2007

For: RUBBER COMPOSITION AND PNEUMATIC TIRE USING THE SAME

Group Art Unit: 1791

Examiner: Justin R. Fischer

Confirmation No.: 9004

DECLARATION UNDER 37 C.F.R. § 1.132

I, Kumi Fujiki, declare that:

I am a co-worker of Mr. Kazunori Kaneda and Mr. Yoshinori Kuriya who are some of the inventors of the above-captioned patent application.

I graduated from Japan Women's University in 1990, and I have been employed by Bridgestone Corporation since 1990, where I have been engaged mainly in research and development of tire materials.

I have made the following experiments in order to show that the rubber composition comprising the derivative of resorcin of the presently claimed invention can provide unexpectedly excellent adhesiveness as compared with the rubber composition comprising the derivative of hydroquinone, i.e., the isomer of resorcin.

Experimental Procedure and Results

The derivatives of resorcin or hydroquinone were synthesized according to the following methods, and the properties thereof were evaluated.

The resulting compounds were analyzed by a high-performance liquid chromatography (HPLC) under the following conditions:

Column: A-312 ODS from YMC Company

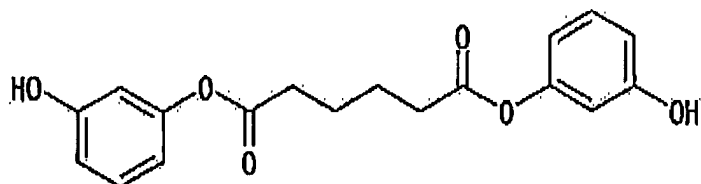
Column temperature: 40°C

Eluting solution: methanol/water = 7/3 (pH is adjusted to 3 with phosphoric acid)

Detection: UV (254 nm)

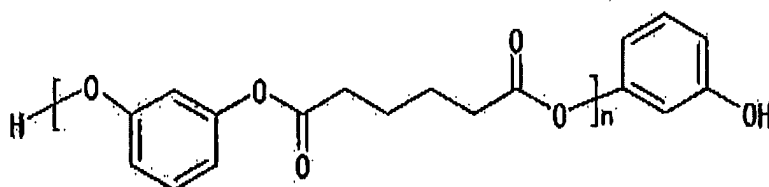
(Production Example A)

A solution of 330.6 g (3.0 mol) of resorcin in 600.0 g of pyridine was kept below 15°C on an ice bath, and 54.9 g (0.30 mol) of adipoyl chloride was gradually dropped into the solution. After the dropping, the temperature of the resulting reaction mixture was raised to room temperature and left to stand over a whole day and night to complete the reaction. From the reaction mixture was distilled off pyridine under a reduced pressure, and the resulting residue was added with 1200 g of water and cooled on ice to precipitate a deposit. The precipitated deposit was filtered and washed with water, and the thus obtained wet body was dried under vacuum to obtain 85 g of a white-light yellow powder. The content of bis(3-hydroxyphenyl) adipate represented by the following formula (I):



... (I)

in the powder was 89% by weight. The powder further contained 7% by weight of a compound represented by the following formula (II):



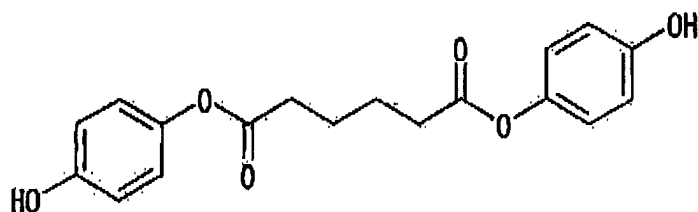
... (II)

wherein  $n$  is 2, 2% by weight of a compound represented by the formula (II), wherein  $n$  is 3, and 2% by weight of resorcin as a starting material.

(Production Example B)

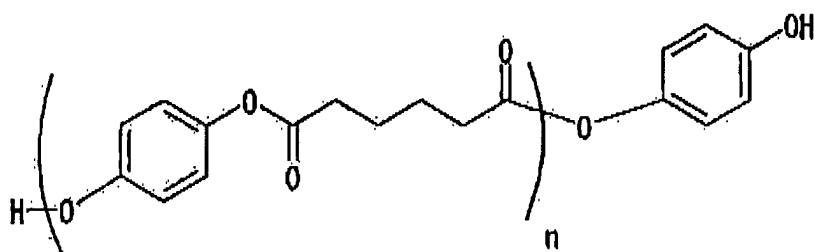
330.6 g (3.0 mol) of hydroquinone was slightly soluble in 600.0 g of pyridine, so that 200.0 g of acetone was further added to fully dissolve. The resulting solution was kept below 15°C on an ice bath, and 54.9 g (0.30 mol) of adipoyl chloride was gradually dropped into the solution. After the dropping, the temperature of the resulting reaction mixture was raised to room temperature and left to stand over a whole day and night to complete the reaction. From the reaction mixture were distilled off pyridine and acetone under a reduced pressure, and the resulting residue was added with 1200 g of water and cooled on ice to precipitate a deposit. The precipitated deposit was filtered and washed with water, and the thus obtained wet body was dried under vacuum to obtain 83 g of a white powder. The content of bis(4-hydroxyphenyl)

adipate represented by the following formula (III):



... (III)

in the powder was 92% by weight. The powder further contained 5% by weight of a compound represented by the following formula (IV):

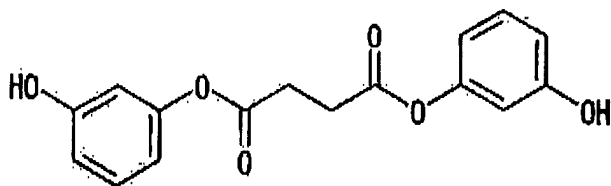


... (IV)

wherein n is 2, and 2% by weight of hydroquinone as a starting material.

#### (Production Example C)

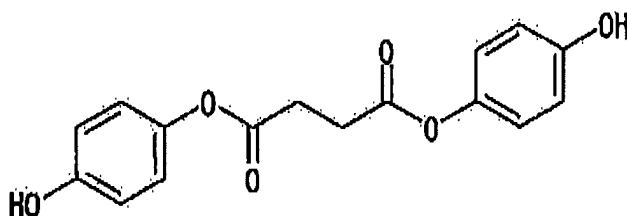
A solution of 440.4 g (4.0 mol) of resorcin in 405.0 g of pyridine is kept below 15°C on an ice bath, and 62.0 g (0.4 mol) of succinyl dichloride is gradually dropped into the solution. After the dropping, the temperature of the resulting reaction mixture is raised to room temperature and left to stand over a whole day and night to complete the reaction. From the reaction mixture is distilled off pyridine under a reduced pressure, and the resulting residue is added with 1800 g of water and cooled on ice, during which the liquid becomes clouded wholly and separates into two phases. The extraction is carried out by adding 200 g of water and 600 g of ethyl acetate to an oil phase. The resulting organic phase is washed five times with cold water and then dried with magnesium sulfate. Thereafter, ethyl acetate is distilled off to obtain a viscous body, which is crystallized by adding 500 g of toluene, filtered, washed with toluene and then subjected to sludging twice with 1L of water. The resulting wet body is dissolved into 100g of methanol, re-precipitated by adding 1L of water, filtered, washed and dried to obtain 82.3 g of light yellow powder. As a result of the HPLC analysis, a primary component of the powder is found to be a component having 91.0 area%. Also, the powder contains 0.7 wt% of resorcin. As a result of structural analysis, the primary component of the powder is found to be bis(3-hydroxyphenyl) succinate represented by the following formula (V):



... (V)

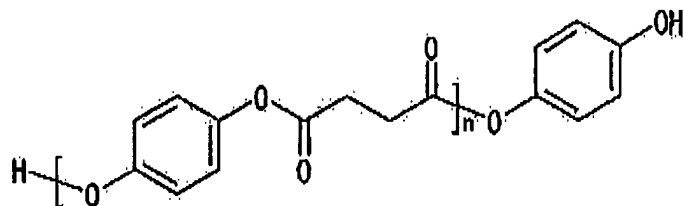
(Production Example D)

77.08 g (0.70 mol) of hydroquinone was slightly soluble in 100.0 g of pyridine, so that 200.0 g of acetone was further added to fully dissolve. The resulting solution was kept below 15°C on an ice bath, and 10.85 g (0.070 mol) of succinyl chloride was gradually dropped into the solution. After the dropping, the temperature of the resulting reaction mixture was raised to room temperature and left to stand over a whole day and night to complete the reaction. From the reaction mixture were distilled off pyridine and acetone under a reduced pressure, and the resulting residue was added with 350 g of water and cooled on ice to precipitate a deposit. The precipitated deposit was filtered and washed with water, and the thus obtained wet body was dried under vacuum to obtain 17.2 g of a white powder. The content of bis(4-hydroxyphenyl) succinate represented by the following formula (VI):



... (VI)

in the powder was 97% by weight. The powder further contained 1% by weight of a compound represented by the following formula (VII):



... (VII)

wherein n is 2, and 0.5% by weight of hydroquinone as a starting material.

(Examples A-D)

Each of the compounds produced in the Production Examples A-D was used as a test.

compound, and mixed and milled with rubber according to a compounding recipe shown in the following Table A to prepare an unvulcanized rubber composition, and then the adhesiveness just after the compounding and adhesiveness after the leaving of compounded rubber were measured and evaluated. The results are shown in the Table A.

(Adhesion test)

Steel cords (1×5 structure, wire diameter: 0.25 mm) plated with brass (Cu: 63 mass%, Zn: 37 mass%) were arranged in parallel to each other at an interval of 12.5 mm and coated with each of the rubber compositions from both sides thereof and immediately vulcanized at 160°C for 15 minutes to prepare a sample having a width of 12.5 mm. After the steel cord was pulled out from the sample according to ASTM-D-2229 for the following adhesiveness, the rubber coated state was visually observed and represented by a value of 0-100% as an indicator of the adhesiveness. The larger the value, the better the property. The initial adhesion was measured just after the vulcanization. The humidity-aged adhesion was measured by aging at 70°C and a humidity of 100% RH for 4 days after the vulcanization.

(Test for adhesion stability)

A steel cord-rubber composite body of an unvulcanized state formed by coating steel cords with each of the rubber compositions was left to stand in a constant temperature and humidity chamber of 40°C and 80% RH for 7 days and then vulcanized at 160°C for 15 minutes to measure an initial adhesion as an indicator of the adhesion stability.

Table A

				Control	Working Example A	Comparative Example B	Working Example C	Comparative Example D
Rubber Formulation	parts by mass			100	100	100	100	100
	Natural Rubber			60	60	60	60	60
	Carbon Black (N326)			5	5	5	5	5
	Sulfur			5	5	5	5	5
	Zinc White			1	1	1	1	1
	Vulcanization Accelerator <sup>1)</sup>			2	2	2	2	2
	Antioxidant <sup>2)</sup>			1	1	1	1	1
	Cobalt Compound <sup>3)</sup>			None	Production Example A	Production Example B	Production Example C	Production Example D
	Test Compound	Sort		-	Resorcin	Hydroquinone	Resorcin	Hydroquinone
				-	Adipoyl chloride	Adipoyl chloride	Succinyl chloride	Succinyl chloride
			0	2	2	2	2	
			100	100	90	100	90	
Evaluation Results	Initial adhesion			%				
	Humidity-aged adhesion			%				
	Adhesion stability			%				

1) N,N'-dicyclohexyl-2-benzothiazyl sulfenamide

[Manufactured by OUCHIISHINKO CHEMICAL INDUSTRIAL CO., LTD., Trade name: NOCCELER DZ]

2) N-phenyl-N'-1,3-dimethylbutyl-p-phenylenediamine

[Manufactured by OUCHIISHINKO CHEMICAL INDUSTRIAL CO., LTD., Trade name: NOCRAC 6C]

3) Manufactured by OMG, Trade name: MANOBOND C22.5

Summary

As seen from Table A, Comparative Examples B and D comprising the derivative of hydroquinone have higher humidity-aged adhesion as compared to Control (additive-free).

However, Working Example A comprising the compound derived from resorcin and adipoyl chloride has further excellent humidity-aged adhesion as compared to Comparative Example B comprising the compound derived from hydroquinone and adipoyl chloride.

Also, Working Example C comprising the compound derived from resorcin and succinyl chloride has further excellent humidity-aged adhesion as compared to Comparative Example D comprising the compound derived from hydroquinone and succinyl chloride.

That is, the results show that the derivative of hydroquinone can improve adhesion; however, the derivative of resorcin can provide unexpectedly more excellent effect on improving adhesion.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: Nov. 10, 2010

Declarant: Kumi Fujiki  
Kumi Fujiki